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Bromobis(Diethyldithiocarbamato)(4-Methoxyphenyl)Tellu

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: VJ1008). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Banerjee, A., Dattagupta, J. K., Saenger, W. & Rabczenko, A. (1977). *Acta Cryst.* B**33**, 90–94.
Banerjee, A., Saenger, W., Lesyng, B., Kazimierczuk, Z. & Shugar, D. (1978). *Acta Cryst.* B**34**, 2472–2477.
Biswas, G., Iitaka, Y., Shugar, D. & Banerjee, A. (1989). *Nucleosides Nucleotides*, **8**, 1335–1343.
Hitchings, G. H., Elion, G. B., Vanderwerff, H. & Falco, E. A. (1948). *J. Biol. Chem.* **174**, 765–767.
Hitchings, G. H., Falco, E. A., Vanderwerff, H., Russel, P. B. & Elion, G. B. (1952). *J. Biol. Chem.* **199**, 43–45.
Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
Mukherjee, M. (1968). PhD thesis, University of Calcutta, India.
Nardelli, M. (1983). *Comput. Chem.* **7**, 95–97.
Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

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Bromobis(diethyldithiocarbamato)-(4-methoxyphenyl)tellurium(IV)

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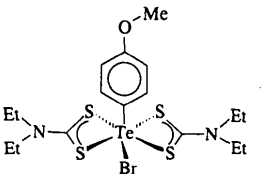
Abstract

The crystals of the Te^{IV} complex p-$CH_3OC_6H_4Te(Et_2NCS_2)_2Br$ are isomorphous with those of the iodine and mixed iodine/bromine analogues previously investigated. The structure is pentagonal bipyramidal at the Te atom with four S atoms [Te—S 2.618–2.721 (1) Å] and the Br atom [Te—Br 2.943 (1) Å] in equatorial positions. The p-methoxyphenyl group is axial [Te—C 2.147 (3) Å]. The second axial position is approached by a Br atom of a centrosymmetrically related complex [Te···Br 3.423 (1) Å, C—Te···Br 173.1 (1)°] so that the molecules are joined into centrosymmetric pairs by this weak secondary coordination.

Comment

The structure of the title complex, (1), is quite similar to the isomorphous structures of the iodo complex p-$MeOC_6H_4Te(Et_2NCS_2)_2I$, (2), and the mixed Br/I complex p-$MeOC_6H_4Te(Et_2NCS_2)_2Br_{0.41}I_{0.59}$, (3), investigated earlier (Husebye, Kudis & Lindeman, 1996*a*). Therefore, the discussion will focus only on those structural parameters of complex (1) which differ significantly from the corresponding structural parameters of (2) and (3), and are an effect of the halogen-atom replacement.



(1)

The Te atom in complex (1) has pentagonal bipyramidal coordination geometry with two bidentate dithiocarbamate ligands and a Br atom in the equatorial plane. There is an aryl group and a secondary bonded Br atom of a centrosymmetrically related complex in axial positions (Fig. 1), so that the molecules of (1) are connected into weakly bound dimers *via* two bridging bromine ligands. This secondary bonding is weaker than in the corresponding iodide [the Te—Br and Te···Br distances differ by 0.480 (1) Å in (1), whereas the Te—I and Te···I distances differ by 0.400 (1) and 0.394 (2) Å in (2) and (3), respectively], in full agreement with the weaker *trans* influence of Br as compared to I. However,

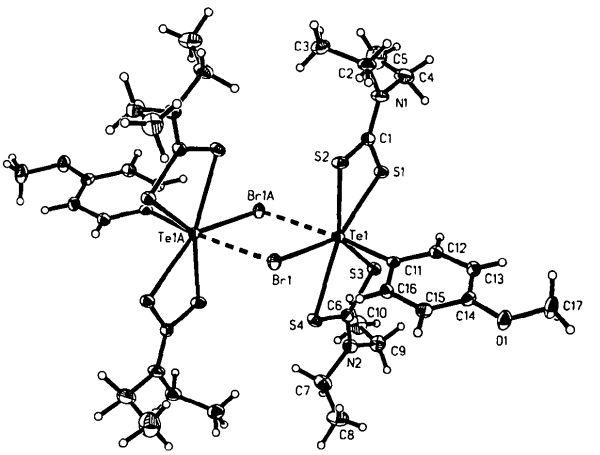


Fig. 1. Perspective view of (1) showing a pair of centrosymmetrically related molecules loosely associated by secondary Te···Br contacts (dashed lines). The displacement ellipsoids are drawn at the 50% probability level.

it is somewhat stronger than we expected. We previously believed that the relatively short secondary intermolecular Te···I contacts had a shortening effect upon the corresponding Te···Br contacts in the mixed complex (3) (Husebye, Kudis & Lindeman, 1996*a*). However, the difference between the Te—Br and Te···Br distances in the ordered crystals of (1) turned out to be less than that found in (3) [0.572 (6) Å]. So the above effect may, on the contrary, be considered rather as a 'loosening' effect. The bond angles C—Te···Br [173.05 (7)°] and Te—Br···Te [89.80 (1)°] have close to 'ideal' values. Such secondary bonding towards 'empty' positions in the coordination sphere of tellurium is quite common in thio and halo complexes (Husebye, 1983; Haiduc, King & Newton, 1994).

The intramolecular Te—Br bond length in (1) [2.943 (1) Å] is noticeably lengthened compared with that found in the closely related complex *p*-$MeOC_6H_4$-$Te(Me_2NCS_2)_2Br$ dichloromethane hemisolvate, (4) [2.890 (1) Å; Husebye, Kudis & Lindeman, 1996*b*], in which the Br atom does not take part in secondary bonding. Nevertheless, the Te—C(Ar) bond in (1), which is located *trans* to the secondary Te···Br bond, has practically the same length [2.147 (3) Å] as in (4) [2.145 (3) Å], where the additional *trans* ligand is not a halogen, but a dithiocarbamate group of a neighbouring molecule acting as a π ligand. So, the *trans* influences of these secondary coordinated ligands seem to be similar.

The *p*-methoxyphenyl ligand has the usual planar π-conjugated structure; the torsion angle C13—C14—O1—C17 is only 3.4 (4)°.

Both dithiocarbamate ligands are quite symmetrically coordinated to the Te atom, but the S atoms in the quasi-*trans* positions to bromine are nearer the Te atom than the atoms in the quasi-*cis* positions: the Te—S1 and Te—S3 distances are 2.619 (1) and 2.618 (1) Å with corresponding Br—Te—S bond angles of 142.45 (2) and 141.09 (2)°, respectively, while Te—S2 and Te—S4 distances are 2.721 (1) and 2.691 (1) Å with Br—Te—S angles of 76.55 (2) and 73.65 (2)°, respectively. These geometric parameters are very close to those found in (2)–(4) and are, evidently, the result of a *trans* influence of the halogen substituent in the equatorial plane.

The Br1—Te1—C11 group forms an approximate mirror plane except for the C3 and C8 methyl groups. The main twist of the aryl plane away from this 'mirror' plane is represented by the Br1—Te1—C11—C16 torsion angle of 15.0 (2)°. The Te atom in (1) is practically in the mean plane of the equatorial substituents, in contrast to the shift of 0.055 (1) Å toward the aryl ligand found in the structure of (2).

The folding of one of the dithiocarbamate chelate rings (S1—C1—S2—Te1) in molecule (1) is less pronounced than in its isomorphous analogue (2) [the folding angles are 8.5 (1) and 12.3 (1)° in (1) and (2), respectively, against the aryl ligand along the line S–S]. The other chelate ring maintains its practically planar conformation [the folding angles are 1.9 (1) and 1.8 (1)° in (1) and (2), respectively]. Both dithiocarbamate ligands have normal π-conjugated structures [the C_{sp^2}—N bond distances are 1.316 and 1.323 (4) Å, the twist about these bonds is no more than 8.8 (2)° and the configuration of the N atoms is planar within 0.030 (3) Å].

In contrast to the isomorphous structures (2) and (3), investigated at room temperature, there is no disorder found at low temperature in the structure of (1): the C4—C5 group, which was disordered in (2) and (3), has only slightly increased atomic displacement parameters and is *syn*-oriented relative to the other ethyl group, like the major components in the disordered structures (2) and (3). The other diethyldithiocarbamate ligand has an *anti*-orientation of the two ethyl groups.

Experimental

The title complex, (1), was synthesized by adding a solution of 1.02 mmol of Br_2 in 3 ml of CCl_4 dropwise to a stirred solution of 1.02 mmol of *p*-$MeOC_6H_4Te(Et_2NCS_2)_3$ in 15 ml of CH_2Cl_2. The stirring was continued for 2 h. A viscous oil slowly formed over two days. The oil was separated and dissolved in 10 ml of ethanol, to which a few drops of CH_2Cl_2 were added. Upon standing, orange–yellow crystals of (1) separated out. Yield based on initial Te compound: 81% (0.504 g).

Crystal data

$C_{17}H_{27}BrN_2OS_4Te$
M_r = 611.16
Monoclinic
$P2_1/n$
a = 9.977 (2) Å
b = 14.009 (3) Å
c = 16.462 (3) Å
β = 91.21 (3)°
V = 2300.3 (8) Å^3
Z = 4
D_x = 1.765 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 11.4–12.6°
μ = 3.403 mm^{-1}
T = 103 (2) K
Prism
0.15 × 0.12 × 0.09 mm
Orange–yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (*MolEN*; Fair, 1990)
T_{min} = 0.286, T_{max} = 0.421
4668 measured reflections
4456 independent reflections
3988 observed reflections [$I > 2\sigma(I)$]
R_{int} = 0.0208
θ_{max} = 25.97°
$h = 0 \rightarrow 12$
$k = 0 \rightarrow 17$
$l = -20 \rightarrow 20$
3 standard reflections
frequency: 120 min
intensity decay: 3.4%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.0278
$wR(F^2)$ = 0.0880
S = 1.028
$(\Delta/\sigma)_{max}$ = 0.017
$\Delta\rho_{max}$ = 1.87 e Å^{-3}
$\Delta\rho_{min}$ = −1.34 e Å^{-3}
Extinction correction: none

4446 reflections
343 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0622P)^2 + 1.3800P]$ where $P = (F_o^2 + 2F_c^2)/3$

Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
Te1	0.07929 (2)	0.592048 (11)	0.899581 (9)	0.01296 (8)
Br1	0.10054 (3)	0.38493 (2)	0.92671 (2)	0.01919 (9)
S1	0.19666 (7)	0.75449 (5)	0.93479 (4)	0.01799 (15)
S2	0.33051 (7)	0.57034 (5)	0.96452 (4)	0.01944 (15)
S3	−0.08252 (6)	0.72006 (5)	0.83570 (4)	0.01698 (14)
S4	−0.14727 (7)	0.51475 (5)	0.83710 (4)	0.01939 (15)
O1	0.3343 (2)	0.5451 (2)	0.55487 (12)	0.0255 (5)
N1	0.4348 (2)	0.7378 (2)	1.00888 (15)	0.0234 (5)
N2	−0.3118 (2)	0.6481 (2)	0.77751 (15)	0.0210 (5)
C1	0.3334 (3)	0.6917 (2)	0.9738 (2)	0.0179 (5)
C2	0.5496 (3)	0.6837 (2)	1.0442 (2)	0.0256 (6)
C3	0.5234 (3)	0.6495 (2)	1.1297 (2)	0.0275 (6)
C4	0.4412 (4)	0.8424 (2)	1.0148 (2)	0.0347 (8)
C5	0.3908 (5)	0.8795 (3)	1.0937 (3)	0.0472 (9)
C6	−0.1948 (3)	0.6289 (2)	0.8122 (2)	0.0175 (5)
C7	−0.4145 (3)	0.5724 (2)	0.7683 (2)	0.0290 (7)
C8	−0.3981 (4)	0.5128 (3)	0.6925 (2)	0.0373 (8)
C9	−0.3505 (3)	0.7450 (2)	0.7515 (2)	0.0250 (6)
C10	−0.4240 (3)	0.7986 (3)	0.8174 (2)	0.0329 (7)
C11	0.1695 (2)	0.5803 (2)	0.7827 (2)	0.0147 (5)
C12	0.2157 (3)	0.6603 (2)	0.7418 (2)	0.0160 (5)
C13	0.2721 (3)	0.6526 (2)	0.6652 (2)	0.0178 (5)
C14	0.2814 (3)	0.5628 (2)	0.6292 (2)	0.0175 (5)
C15	0.2350 (3)	0.4824 (2)	0.6701 (2)	0.0211 (6)
C16	0.1798 (3)	0.4911 (2)	0.7464 (2)	0.0182 (5)
C17	0.3909 (4)	0.6241 (2)	0.5123 (2)	0.0297 (7)

Table 2. *Selected geometric parameters (Å, °)*

Te1—C11	2.147 (3)	S4—C6	1.715 (3)
Te1—S3	2.6184 (8)	O1—C14	1.366 (3)
Te1—S1	2.6187 (8)	O1—C17	1.433 (4)
Te1—S4	2.6910 (9)	N1—C1	1.323 (4)
Te1—S2	2.7211 (10)	N1—C4	1.470 (4)
Te1—Br1	2.9427 (7)	N1—C2	1.482 (4)
Te1···Br1^i	3.4229 (10)	N2—C6	1.316 (4)
S1—C1	1.735 (3)	N2—C9	1.473 (4)
S2—C1	1.707 (3)	N2—C7	1.480 (4)
S3—C6	1.737 (3)		
C11—Te1—S3	87.67 (7)	Te1—Br1···Te1^i	89.801 (9)
C11—Te1—S1	94.06 (7)	C1—S1—Te1	89.18 (10)
S3—Te1—S1	76.27 (3)	C1—S2—Te1	86.41 (9)
C11—Te1—S4	89.51 (7)	C6—S3—Te1	88.58 (10)
S3—Te1—S4	67.44 (3)	C6—S4—Te1	86.66 (9)
S1—Te1—S4	143.36 (2)	C14—O1—C17	117.5 (2)
C11—Te1—S2	86.75 (7)	C1—N1—C4	123.2 (3)
S3—Te1—S2	142.12 (2)	C1—N1—C2	119.9 (2)
S1—Te1—S2	66.81 (2)	C4—N1—C2	116.8 (2)
S4—Te1—S2	149.83 (2)	C6—N2—C9	122.6 (2)
C11—Te1—Br1	91.73 (7)	C6—N2—C7	120.3 (3)
S3—Te1—Br1	141.09 (2)	C9—N2—C7	117.0 (2)
S1—Te1—Br1	142.45 (2)	N1—C1—S2	122.5 (2)
S4—Te1—Br1	73.65 (2)	N1—C1—S1	120.1 (2)
S2—Te1—Br1	76.55 (2)	S2—C1—S1	117.4 (2)
C11—Te1···Br1^i	173.05 (7)	N2—C6—S4	122.1 (2)
S3—Te1···Br1^i	86.64 (2)	N2—C6—S3	120.6 (2)
S1—Te1···Br1^i	88.46 (2)	S4—C6—S3	117.3 (2)
S4—Te1···Br1^i	84.63 (2)	C16—C11—C12	119.2 (2)
S2—Te1···Br1^i	100.20 (3)	C16—C11—Te1	119.4 (2)
Br1—Te1···Br1^i	90.197 (9)	C12—C11—Te1	121.5 (2)
C11—Te1—Br1···Te1^i	−173.32 (7)	S3—Te1—C11—C16	−126.1 (2)
Te1—S2—C1—S1	−4.08 (14)	S1—Te1—C11—C16	157.8 (2)
Te1—S1—C1—S2	4.24 (15)	S4—Te1—C11—C16	−58.7 (2)
Te1—S4—C6—S3	1.48 (14)	S2—Te1—C11—C16	91.4 (2)
Te1—S3—C6—S4	−1.52 (15)	Br1—Te1—C11—C12	−166.3 (2)

Symmetry code: (i) $-x, 1-y, 2-z$.

Refinement was on F^2 for all reflections except for 10 flagged by us for potential systematic errors.

Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1340). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.

Haiduc, I., King, R. B. & Newton, M. G. (1994). *Chem. Rev.* **94**, 301–326.

Husebye, S. (1983). *Proceedings of the Fourth International Conference on the Organic Chemistry of Selenium and Tellurium*. University of Aston, England, edited by F. J. Berry & W. R. McWhinnie, pp. 298–378.

Husebye, S., Kudis, S. & Lindeman, S. V. (1996*a*). *Acta Cryst.* C**52**, 424–429.

Husebye, S., Kudis, S. & Lindeman, S. V. (1996*b*). *Acta Cryst.* C**52**, 429–432.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1993). *SHELXL*93. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

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Rhoiptelenyl Acetate, a New Pentacyclic Triterpenoid from *Ficus thunbergii*

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Abstract

Rhoiptelenol, (2), isolated from *Ficus thunbergii* Maxim. (Moraceae), has been reported as a triterpenoid component. The title compound, (1), whose molecular formula was shown by its high-resolution mass spectrum to be $C_{32}H_{52}O_2$, was obtained from (2) by acetylation with Ac_2O and pyridine. The structure of (1) was